

SOME EFFECTS OF FILTRATION ON THE DETERMINATION OF COPPER IN FRESHWATER AND SALTWATER¹

ABSTRACT

Analysis of variance calculations were made to interpret the effects of filtration, initial copper concentration, and type of water on the concentration of copper in filtered samples of freshwater and saltwater. Five types of filters were tested. Filtration constituted a significant source of variation. Each filter tested reduced the reliability of the copper determination.

INTRODUCTION

Natural waters are complex solutions containing many elements, often at very low concentrations that are difficult to measure accurately. Much of the discrepancy in the literature concerning the concentration of trace elements in seawater may be a result of sample contamination. Quantitative filter papers always contain metal contamination and may adsorb such metals as lead and copper (Sandell 1950). Robertson (1968) investigated the role of

contamination in the trace element analysis of seawater and showed that many materials used in the collection and treatment of water samples contain high levels of impurities of various elements.

We have investigated filtration effects on copper concentrations in freshwater and saltwater. Samples often are filtered before chemical examination, as, for example, before the colorimetric analysis of turbid waters. We have demonstrated the effects of five types of filters, each of which altered the composition of the sample and thus affected the reliability of the analyses.

PROCEDURE

The effect of filtration was determined by measuring the copper in filtered and unfiltered portions of freshwater and saltwater samples. The freshwater was double-distilled from tap water in an all-glass still, and the saltwater was taken from East Lagoon on Galveston Island. Because both waters were virtually copper-free, portions of a standardized copper sulfate solution

¹ Contribution No. 294 from the Bureau of Commercial Fisheries Biological Laboratory, Galveston, Texas 77550.

TABLE 1. *Copper analyses of filtered* and unfiltered water (units: absorbance $\times 100$)*

Test level ($\mu\text{g-atom}$ Cu/liter)	Freshwater						Saltwater					
	F ₀	F ₁	F ₂	F ₃	F ₄	F ₅	F ₀	F ₁	F ₂	F ₃	F ₄	F ₅
Block 1												
0	0.0	0.2	0.2	0.1	2.2	0.2	0.5	1.1	1.1	0.8	2.3	0.5
1	10.5	4.1	2.2	0.2	11.8	0.2	11.8	10.2	10.2	5.1	13.6	3.2
2	18.9	6.3	4.6	0.5	15.1	0.3	18.0	16.5	16.3	8.5	21.2	4.3
3	28.0	14.3	6.5	2.0	14.1	1.0	28.1	24.8	24.6	16.7	32.0	7.9
4	36.8	17.7	10.2	2.0	27.7	4.5	40.3	29.8	31.2	17.5	32.9	7.5
5	47.8	31.3	21.0	8.6	47.1	12.8	47.8	39.6	40.9	22.0	45.5	7.5
Block 2												
0	0.0	2.2	2.2	1.7	6.4	1.0	0.6	2.6	2.7	2.7	5.5	1.3
1	11.8	11.1	11.1	2.3	17.7	8.5	7.9	9.8	9.2	7.0	13.1	2.8
2	21.6	8.5	5.2	3.3	22.3	1.5	14.5	16.3	13.6	12.9	18.4	3.4
3	29.7	10.8	5.0	2.6	33.8	1.3	27.4	25.5	25.0	16.0	38.4	5.8
4	38.8	20.2	11.4	4.4	27.6	5.4	36.7	32.0	41.2	20.3	40.5	0.6
5	46.6	22.9	15.2	10.8	44.7	8.8	48.0	40.0	40.0	28.0	47.2	7.2
Block 3												
0	0.1	3.0	1.5	1.0	3.4	0.9	0.0	2.2	1.1	1.6	9.6	1.9
1	9.4	4.4	3.0	1.2	9.5	1.7	9.3	7.5	8.5	6.2	14.3	2.5
2	18.5	8.9	4.2	3.4	22.2	0.6	9.9	10.9	11.0	6.7	12.1	1.6
3	27.0	13.5	6.9	2.7	28.0	2.9	16.0	14.2	15.0	13.0	18.3	2.0
4	35.5	17.3	9.9	7.3	29.0	11.2	31.5	30.2	27.3	14.9	25.7	2.8
5	44.0	21.0	13.0	11.9	33.0	11.1	40.0	37.1	37.0	25.9	47.0	5.0
Block 4												
0	0.0	0.5	1.0	1.0	3.6	0.4	0.0	2.5	0.7	0.1	6.1	0.3
1	10.8	3.6	3.0	1.4	5.4	0.4	9.0	7.9	7.0	6.9	11.0	1.8
2	20.0	7.0	2.6	1.4	22.5	0.2	15.0	11.8	12.7	8.9	18.7	1.9
3	29.3	13.0	6.6	10.0	25.0	2.9	23.8	19.4	20.9	17.4	29.2	3.2
4	38.0	16.8	11.6	5.8	39.7	7.3	32.4	30.2	26.2	18.0	38.0	4.0
5	45.5	16.3	10.2	2.7	48.6	4.5	41.0	32.6	35.1	27.1	45.9	3.8

* Filter: F₀—none; F₁—unwashed paper (Whatman No. 1); F₂—acid-washed paper (Whatman No. 40); F₃—glass wool; F₄—membrane (Gelman GA-4); F₅—sintered glass.

were added 24 hr before analysis to obtain concentrations from 0 to 5 $\mu\text{g-atom Cu/liter}$.

Each sample was divided into 6 subsamples (Table 1), and portions were analyzed for copper before and after filtration with each of five types of filters. The experiment was repeated on each of 4 days with each set made on separate samples of water.

The five filter materials were:

1. Untreated filter paper (Whatman No. 1, 18.5-cm diam).
2. Acid-washed filter paper (Whatman No. 40, 18.5-cm diam).
3. Borosilicate glass wool with fibers ranging from 5 to 8 μ .
4. Cellulose acetate microporous mem-

brane filters (Gelman GA-4, 10.2-cm diam, pore size 0.8 μ).

5. Sintered-glass disk (8.9-cm diam, pores ranging from 10 to 15 μ).

Except for the sintered-glass disk, each filter was used only once. The paper and membrane filters were folded to fit 60° glass funnels; the membranes were softened in distilled water before folding. The glass-wool filters were prepared by packing 4 g of the fiber into funnels tightly enough so that a portion of the wool extended into the stem of the funnels. The sintered-glass disk was cleaned before each filtration by filtering, with the aid of suction, 100 ml of concd HCl and thirty 100-ml portions of distilled water through the disk.

Concentrations of copper were deter-

TABLE 2. Summary of analyses of variance calculations

Source of variation	df	Σx^2	s^2	F
Freshwater and saltwater samples				
Blocks	3	313.82	104.60	10.86*
Concentration	5	23,412.82	4,682.56	486.25*
Filters	5	14,645.72	2,929.14	304.17*
Water	1	1,533.19	1,533.19	159.21*
(Concn \times filters)	25	5,809.83	232.39	24.13*
(Concn \times water)	5	631.07	126.21	13.11*
(Filter \times water)	5	1,960.59	392.11	40.72*
(Concn \times filter \times water)	25	1,035.20	41.40	4.30*
Error	213	2,052.60	9.63	
Total	287	51,394.84		
Freshwater samples				
Blocks	3	78.22	26.07	2.53
Concentration	5	8,236.42	1,647.28	160.24*
Filters	5	9,828.40	1,965.68	191.21*
(Concn \times filters)	25	3,732.50	149.30	14.52*
Error	105	1,078.98	10.28	
Total	143	22,954.52		
Saltwater samples				
Blocks	3	367.94	122.64	15.31*
Concentration	5	15,807.47	3,161.49	394.69*
Filters	5	6,777.91	1,355.82	169.26*
(Concn \times filters)	25	3,112.54	124.50	15.54*
Error	105	841.27	8.01	
Total	143	26,907.13		

* Significant at the 1% level.

mined by a biquinoline method (Hoste, Eeckhout, and Gillis 1953). Before analysis, the pH of all samples was adjusted to 8.0–8.6 with a buffer of barbitol-sodium barbitol. Absorbance was read at 525 m μ (525 B glass filter) in 3-ml microcells in an electrophotometer.

Paper and membrane filters were also analyzed to determine variation of their copper concentration before and after use. They were prepared for analysis by digestion in a mixture of 3 parts of concd nitric acid, 1 part of concd sulfuric acid, and 1 part of 70% perchloric acid. The acid mixtures were evaporated to about 10% of their initial volumes, cooled, and neutralized (litmus paper indicator) with sodium hydroxide. These solutions were then diluted with distilled water to about 50 ml,

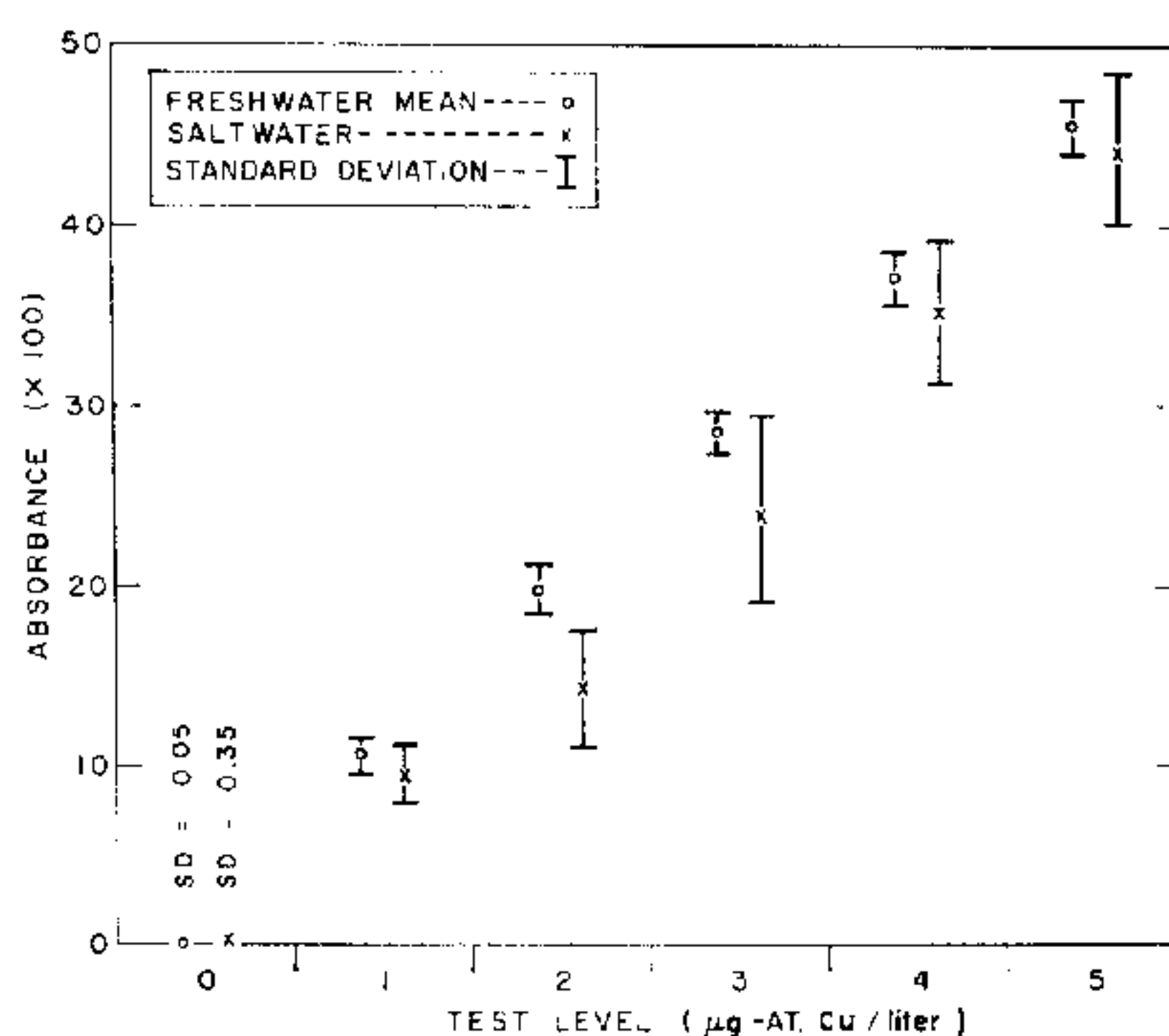


FIG. 1. Mean copper concentration of unfiltered water at 6 test levels.

buffered to the desired pH, and diluted to a volume of 100 ml before analysis.

The results of copper analyses of the water samples are shown in Table 1. The erratic values reflect, we believe, variation of filter effect with filter type. Copper analyses are shown as absorbance \times 100. The relation between this unit and the more conventional concentration unit, μ g-atom Cu/liter, can be seen by comparing the absorbance units with the test levels (μ g-atom Cu/liter) in Table 1. Because the relation is weak after some of the filter treatments, no attempt was made to convert absorbance units to μ g-atom Cu/liter.

SOURCES OF ERROR

Analysis of variance calculations were performed to evaluate the effects of the filters, initial concentrations of copper, and types of water on the concentration of copper in the filtered samples (Table 2). Each daily set of analyses was treated as a block.

There was a large amount of daily variation in the saltwater samples but not in the freshwater samples; consequently, separate analyses were performed for freshwater and saltwater (Table 2).

Blocks

Differences between determinations made on different days (blocks) were significant

TABLE 3. Mean copper concentration (absorbance $\times 100$) of samples after each treatment*

Filter treatment	Freshwater	Saltwater
None	23.69	21.23
Membrane	22.49	24.43†
Untreated paper	11.45†	18.95
Acid-washed paper	7.01†	19.02
Glass wool	3.68†	12.68†
Sintered glass	3.73†	3.45†

* Results of Tukey's test which show the least significant difference between means (5% level) to be: freshwater, 2.85; saltwater, 2.52.

† Significantly different from unfiltered water mean.

at the 1% level when all data were combined but were not significant at that level for the freshwater data alone (Table 2).

Because samples at the 6 test levels were analyzed on each of 4 days, each mean represents 4 analyses. If no analytical differences existed between days and water types, the saltwater and freshwater analyses at a given concentration of copper should give identical results. Each saltwater mean, however, with the exception of that at 0 concentration, is less than the corresponding freshwater mean (Fig. 1). These differences and the fact that the standard deviations are greater for the 4 analyses of saltwater than for the corresponding freshwater analyses suggest that either the freshwater or saltwater data are biased.

The probability of bias is much lower in the data for freshwater than for saltwater because the 4 freshwater samples were actually subsamples of our entire supply of double-distilled water (about 200 liters). The copper treatment was identical, so the 4 samples were, for all practical purposes, replicates.

The saltwater samples, however, were not necessarily replicates because soluble copper has a tendency to precipitate as a basic carbonate in saltwater, the amount varying with pH and salinity (Ferry 1952). This could account for the low mean values for saltwater shown in Fig. 1; although the saltwater and freshwater samples were virtually identical in total copper content, they did not necessarily contain the same amounts of detectable copper (the copper

analysis does not detect un-ionized copper). We believe that variations in pH and salinity on the 4 samplings days caused the high standard deviations for the saltwater data.

Concentration

A significant proportion of the variation was associated with differences in the concentration of copper in the test solutions. This expected variation was removed so effects of other factors could be recognized.

Filters

The effects of filters were significantly different at the 1% level (Table 2). The least significant difference between the mean levels of copper concentration of all the samples filtered, at the 5% confidence level, was calculated by using Tukey's test (Table 3). Average values of copper in freshwater filtered through a membrane and in saltwater filtered through paper (both untreated and acid-washed), when compared with the means for the remaining filters, could not be distinguished from those obtained from unfiltered water.

The data in Table 4 suggest that the filters themselves are contaminated with copper, to a degree that can be increased by sample sorption or decreased by sample elution. If this assumption is true, changes in the copper concentration of samples and in the filtering material after filtration should be opposite but of equal magnitude.

We conducted three experiments, all with freshwater, to determine the distribution of copper in sample-filter systems before and after filtration. Two experiments were with samples to which copper had been added—one with the untreated paper filter and the other with the acid-washed paper filter—and the third was with copper-free water and the membrane filter. The amount of copper gained or lost by the filters and the corresponding losses or gains of copper by the filtrate were examined using "Student's" *t*-tests (Davies 1954; Table 5). Results confirm that the filters were contaminated with enough copper to account for the increases in copper concen-

TABLE 4. Mean copper concentrations detected in the 4 sets of analyses at each test level after each treatment*

Test level	Freshwater						Saltwater					
	F ₀	F ₁	F ₂	F ₃	F ₄	F ₅	F ₀	F ₁	F ₂	F ₃	F ₄	F ₅
0	0.0	1.5	1.2	1.0	3.9	0.6	0.3	2.1	1.4	1.3	5.9	1.0
1	10.6	5.8	4.8	1.3	11.1	2.7	9.5	8.8	8.7	6.3	13.0	2.6
2	19.8	7.7	4.2	2.2	20.5	0.6	14.4	13.9	13.4	9.2	17.6	2.8
3	28.5	12.9	6.2	4.3	25.2	2.0	23.8	21.0	21.4	15.8	29.4	4.7
4	37.3	18.0	10.8	4.9	30.8	7.1	35.2	30.6	31.5	17.7	34.3	3.7
5	46.0	22.9	14.8	8.5	43.4	9.3	44.2	37.3	37.8	25.8	46.4	5.9

* Type of filter: same as Table 1.

tration of the sample filtrates (Table 4) and that the filters absorbed sufficient copper to account for the decreases.

The glass filters were not included in this series of tests because of difficulties involved in the analysis of this material. We believe, however, that results from systems that included the two glass filters would be similar to those with paper filters.

Water

The average concentration of copper in filtered saltwater was higher than that in filtered freshwater (Table 3), indicating a greater loss of copper from freshwater during filtration. Exceptions were samples that were filtered through sintered glass.

Interactions

All interactions between main factors were significant at the 1% level (Table 2). The interaction between concentration and filters indicates that the effect of some filters on the copper concentration is dependent on the initial copper concentration of the sample.

The interaction between water type and copper concentration is seen by comparing values of unfiltered freshwater with those of unfiltered saltwater at each test level (Fig. 1). The variable difference between these two sets of means are indicative of an interaction.

The filter \times water interaction is significant at the 1% level and indicates a difference between the action of the individual filters when used with freshwater and saltwater.

The three-way interaction can be seen by comparing the data in Fig. 2 with those in Fig. 1. The fact that each saltwater mean is greater than the corresponding freshwater mean in Fig. 2, whereas the reverse is true in Fig. 1, indicates the concentration \times filter \times water interaction.

RELATION OF FILTRATION TO ANALYSIS FOR TRACE ELEMENTS

In our investigation filtration was a major source of variation affecting the reliability of a copper analysis, some caused by copper contamination of the filter and some

TABLE 5. Concentration of copper in freshwater and filters before and after filtration

Statistic	1. Sample + copper*		Untreated paper filter†		2. Sample + copper		Acid-washed paper filter		3. Copper-free sample		Membrane filter	
	F	U	U	N	F	U	U	N	F	U	U	N
N	8	8	8	8	8	8	8	8	6	6	6	6
\bar{X}	34.84	14.85	27.17	5.53	38.86	10.45	29.10	1.69	0.13	3.40	6.25	9.05
Diff.	-19.99		21.84		-28.41		27.41		3.27		-2.80	
"Student's" t			1.49				1.82				1.82	
$t_{(0.05)}$			2.14				2.14				2.23	

* F = filtered; U = unfiltered.

† U = used; N = new.

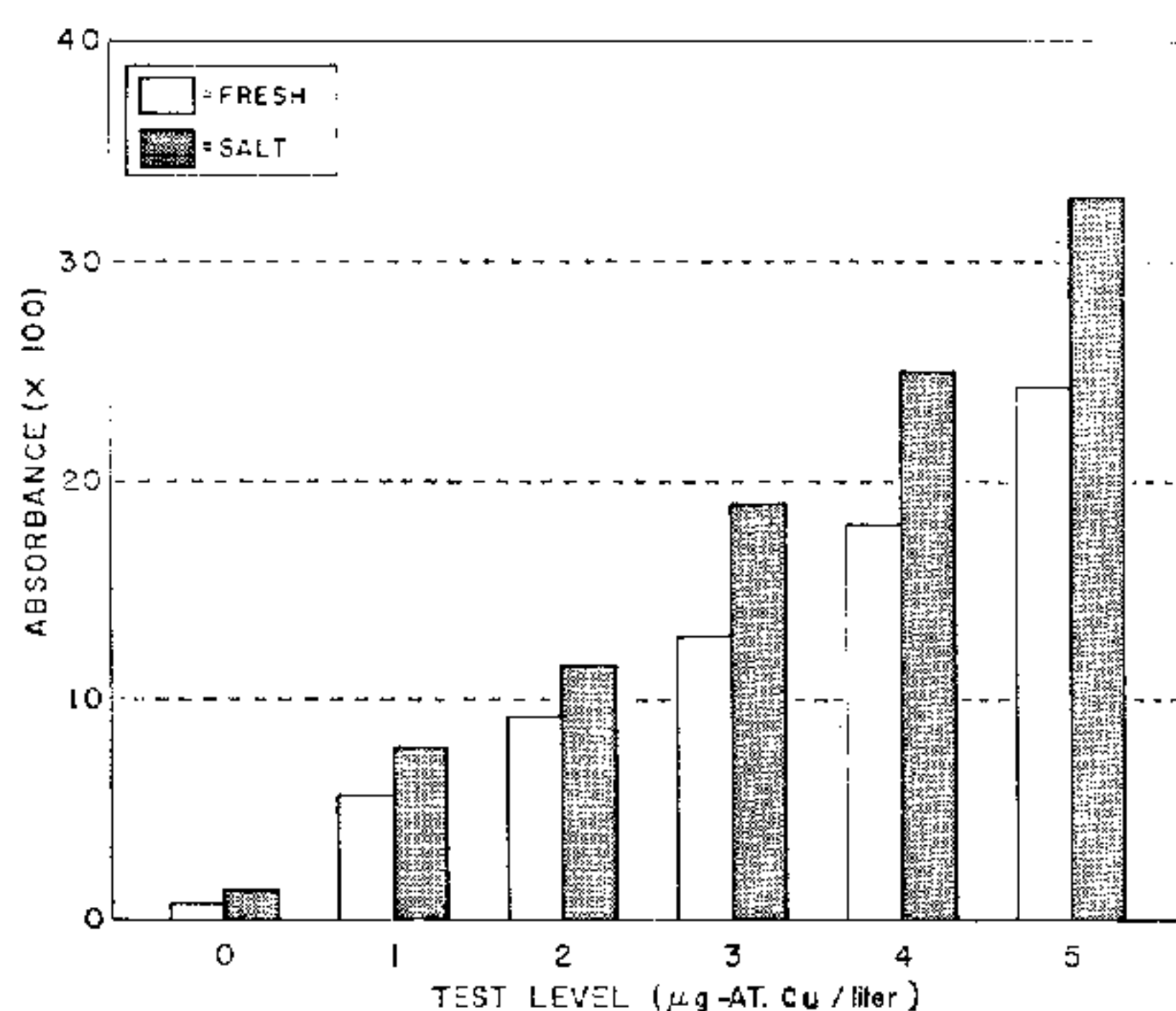


FIG. 2. Mean copper concentration of filtered freshwater and saltwater samples at 6 test levels.

by copper adsorption by the filter media. At copper concentrations of less than 1.0 $\mu\text{g-atom/liter}$, such as those normally encountered in seawater, the membrane filter altered the copper concentration of samples more than did any of the others. Conversely, the glass filters (overall the most objectionable ones tested) were the least objectionable at natural concentrations.

At the higher levels tested, representative of those encountered during dinoflagellate control experiments in coastal waters (Rounsefell and Evans 1958), the effects of copper absorption by the filters were greater than the effects of contamination (Table 4). The one exception was the membrane filter, which increased the copper concentration of most of the saltwater samples.

The variation of filter effects with water type emphasizes the importance of testing prospective filter material at a wide range of concentrations.

Some of the results of this investigation corroborate those reported by others. Sandell (1950) questioned the use of paper filters because of their contaminating and absorption characteristics and also stated that inorganic filters are generally preferable to paper filters for trace element analyses. Our results indicate that his generalized statement about inorganic filter media may not always apply for copper analyses. At least two inorganic filters—glass wool and sintered glass—can seriously affect the reliability of a copper analysis.

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